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⑩ Production of difluoromethane.

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**Description**

This invention relates to a process for the production of difluoromethane.

In recent years chlorofluorocarbons, which are used on a large scale around the world, have been perceived as having an adverse effect on the ozone layer and/or as contributing to global warming. Chlorofluorocarbons are used, for example, as refrigerants, as foam blowing agents, as cleaning solvents and as propellants for aerosol sprays in which the variety of applications is virtually unlimited. Consequently, much effort is being devoted to finding suitable replacements for chlorofluorocarbons which will perform satisfactorily in the many applications in which chlorofluorocarbons are used but which will not have the aforementioned environmentally harmful effects. One approach in the search for suitable replacements has centred on fluorocarbons which do not contain chlorine but which may contain hydrogen. The hydrofluorocarbon difluoromethane, also known as HFA 32, is of interest as one such replacement, in particular as a replacement in refrigeration, air-conditioning and other applications.

According to the present Invention there is provided a process for the production of difluoromethane which comprises reacting a compound of formula  $XYCF_2$  wherein X and Y are each H, Cl or Br but at least one of X and Y is an atom other than hydrogen, with hydrogen at elevated temperature in the presence of a hydrogenation catalyst.

The process may be conveniently effected by feeding a stream comprising the compound of formula  $XYCF_2$  and hydrogen, as a combined or as separate streams through a vessel containing the hydrogenation catalyst.

The starting compounds of formula  $XYCF_2$  are dichlorodifluoromethane, dibromodifluoromethane, chlorobromodifluoromethane, chlorodifluoromethane and bromodifluoromethane. Mixtures of the above compounds may be employed. Usually the compound of formula  $XYCF_2$  will be a chlorinated difluoromethane and chlorodifluoromethane is the preferred starting compound.

Where the compound of formula  $XYCF_2$  is chlorodifluoromethane, we have found that the yield of difluoromethane is dependent upon the catalyst composition, temperature and pressure, and that these parameters may be selected to give surprisingly high yields of difluoromethane, and in particular, substantially higher yields of difluoromethane than the yields which have previously been achieved by hydrogenation of chlorine-containing difluoromethanes.

Accordingly the present invention further provides a process for the production of difluoromethane which comprises contacting chlorodifluoromethane with hydrogen in the presence of a hydrogenation catalyst wherein the temperature, pressure and catalyst composition are such that difluoromethane is produced with a yield of at least 20%. Preferably the yield is at least 25%, more preferably at least 30% and especially at least 35%.

Hydrogenation catalysts are in themselves well known. Examples of hydrogenation catalysts include nickel or metals of Group VIIIa of the Periodic Table, for example platinum, ruthenium, osmium, iridium and rhodium, or oxides or salts thereof. In use, a compound of such a metal is reduced at least in part to the metal. One very useful metal which can be employed is palladium, and we prefer to employ a catalyst which comprises palladium. The metal may, and usually will, be carried on a suitable support, for example, alumina, silica or carbon. A particularly preferred metal/support combination is palladium on an active carbon.

Furthermore, the catalyst may comprise more than one metal which may be carried on a suitable support. Where more than one metal is carried on the support, we generally prefer that one of the metals is palladium. The other metal is preferably a more active hydrogenation catalyst than palladium and the other metal serves to hydrogenate any chlorofluoromethane which may be produced by the process, and which is a toxic impurity, to methane. We have found that the provision of a metal other than palladium, in addition to palladium, may reduce the level of chlorofluoromethane in the product stream without significantly reducing the overall yield of difluoromethane. Thus, the provision of a more active hydrogenation catalyst than palladium, in addition to palladium, acts to purify the product stream by hydrogenation of the toxic impurity, chlorofluoromethane, to methane.

The catalyst may comprise palladium and one or more other group VIIIa metals, for example ruthenium, rhodium or nickel, or other metals, for example silver or chromium, carried on a suitable support. A particularly preferred catalyst comprises palladium and nickel, since we have found that a catalyst comprising palladium and nickel has a profound effect in reducing the amount of the toxic impurity chlorofluoromethane which is present in the product stream. The palladium and nickel may be carried on a support, preferably an active carbon. Each may be carried on the same support, for example an active carbon or on different active carbon supports. Where they are carried on the same support, they may be present as an alloy, if desired.

We have also found that where the support is an active carbon, the overall yield of difluoromethane is profoundly influenced by the particular active carbon which is employed.

According to a further aspect of the present invention there is provided a process for the production of difluoromethane which comprises contacting chlorodifluoromethane with hydrogen in the presence of a catalyst comprising palladium carried on an active carbon support at elevated temperature wherein the active carbon is such that at a temperature of 300 °C, at atmospheric pressure, with a 2:1 molar excess of hydrogen to chlorofluoromethane and with a palladium loading on the active carbon of 8% w/w (whether or not other metals are also present), the yield of difluoromethane is at least 20%. Preferably the yield of difluoromethane is at least 25%, more preferably at least 30% and especially at least 35%.

Whilst it is believed that an important characteristic of the active carbon in determining its effectiveness is the surface area of the carbon, it is clear that other factors are also important including for example acidity, bulk density, the presence of impregnants, the nature of the carbon which is activated and its method of manufacture. Certain active carbons have a demonstrable effect upon the selectivity of the catalyst towards the production of difluoromethane. One type of active carbon which we have found particularly preferably is active carbons which have been manufactured by extrusion.

In the majority of supported catalysts, the loading of the metal on the support material may be dependent at least to some extent on the particular metal catalyst/support combination being used. However the % w/w catalyst to support is typically from 0.1% w/w to 40% w/w, and where the catalyst/support combination comprises palladium supported on an active carbon, the % w/w Pd to active carbon is usually from 5.0% w/w to 20% w/w, preferably from 8.0% w/w to 20% w/w, and especially from 8% w/w to 15% w/w.

In the case where a mixed metal catalyst is employed the proportions of the metals present may vary within a wide range, although generally we prefer to employ a catalyst which is based on palladium. Generally we prefer to employ a catalyst in which there is at least twice as much palladium present as other metals. Where the catalyst comprises a mixture of palladium and nickel, we prefer to employ palladium and nickel in the ratio from 2:1 to 500:1, and more preferably from 5:1 to 100:1. A preferred catalyst comprises from 0.5% to 20%, in particular from 5 to 15% w/w palladium and from about 0.05% to 5%, in particular from 0.1% to 2% by weight nickel, supported on an active carbon. Overall the amount of the metal which is a more active hydrogenation catalyst than palladium, is usually in the range from 0.01% w/w to 5% w/w.

The proportion of hydrogen to starting compound of formula XYCF<sub>2</sub> may be varied considerably. Usually at least the stoichiometric amount of hydrogen is employed to replace the chlorine and/or bromine atom(s), and considerably greater than stoichiometric amounts, for example 4 or more moles of hydrogen per mole of starting compound may be employed. Where X and Y are each chlorine or bromine, it is preferred to employ at least two moles of hydrogen (the stoichiometric amount) per mole of starting compound. Where the starting compound of formula XYCF<sub>2</sub> is chlorodifluoromethane it is preferred to employ between 1 and 2 moles of hydrogen per mole of chlorodifluoromethane.

Atmospheric or superatmospheric pressures, for example up to 80 bars may be employed. We have found that operation of the process of the invention at superatmospheric pressure substantially increases the selectivity of the process towards the production of difluoromethane. The process is preferably operated at a pressure in the range from 2 bar to 60 bar and more preferably from 2 bar to 30 bar, especially 5 bar to 30 bar.

The reaction is suitably carried out in the vapour phase at a temperature which is at least 150 °C and not greater than 450 °C, usually from 225 °C to 400 °C, and preferably from 240 °C to 360 °C. The most preferred temperature is dependent upon the pressure at which the process is operated; at atmospheric pressure, we prefer to operate the process at a temperature in the range from 220 °C to 320 °C, whereas at a pressure of 7.5 bar, we prefer to employ temperatures in the range from 270 °C to 360 °C.

Contact times are usually in the range 1 to 60 seconds, especially 5 to 30 seconds, when the reaction is carried out in the vapour phase.

In the present process, any unreacted hydrogen and other starting material, together with any organic by-products, may be recycled.

The difluoromethane product may be contaminated with small amounts of by-products, for example chlorofluoromethane, chloromethane, fluoromethane and methane. Many of these by-products may be removed by conventional means, for example by fractional distillation. However, one by-product which may be produced is chlorofluoromethane which must be removed or at least reduced to extremely low levels, for example below 10ppm, because it is toxic. Although chlorofluoromethane has a different boiling point to that of difluoromethane, so that they may be separated to a high degree by conventional means, for example by distillation, such conventional processes do not sufficiently reduce the levels of the chlorofluoromethane impurity.

We have found that the chlorofluoromethane and other chlorine containing impurities may be removed from the difluoromethane product by contacting the impure difluoromethane with an active carbon.

According to a further embodiment of the invention there is provided a process for the production of difluoromethane which comprises reacting a compound of formula  $XYCF_2$  wherein X and Y are each H, Cl or Br but at least one of X and Y is an atom other than hydrogen, with hydrogen at elevated temperature in the presence of a hydrogenation catalyst to produce difluoromethane and wherein chlorocarbon impurities are removed from the difluoromethane by contacting the impure difluoromethane with an active carbon. A preferred embodiment is characterised by the removal of chlorofluoromethane from difluoromethane by contacting the impure difluoromethane with an active carbon.

10 The invention is illustrated, but not limited, by the following examples.

#### EXAMPLE 1.

15 60mls of a catalyst comprising 0.84% w/w palladium supported on charcoal (Grade 208c supplied by Sutcliffe Speakman Ltd) were charged into a heat resistant glass tube reactor of 1 inch internal diameter surrounded by an electric furnace.

Hydrogen and chlorodifluoromethane were passed through the heated tube, the catalyst bed being maintained at an essentially constant temperature. Four runs were carried out at the temperatures shown in Table 1 below. The flow rates of hydrogen and chlorodifluoromethane were 60ml/minute and 30ml/minute 20 respectively.

The reactor exit gas was diluted with 300ml/minute nitrogen and passed through a scrubbing tower of soda lime to remove acid gases. The scrubbed exit gas was then analysed by gas chromatography. The relative amounts of the only organic products detected in the scrubbed exit gas, based upon gas chromatogram peak areas only, were as shown in Table 1.

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TABLE 1

Product.	Temperature/ °C.			
	261	334	357	386
CH <sub>2</sub> F <sub>2</sub> .	5.47	21.64	21.07	21.82
CH <sub>4</sub> .	2.15	31.22	44.59	57.92
CF <sub>3</sub> H.	0.11	0.25	0.10	0.13
CH <sub>2</sub> Cl.	-	-	0.24	0.42
CH <sub>3</sub> CH <sub>3</sub> .	-	0.88	2.44	4.15
CF <sub>2</sub> Cl <sub>2</sub>	-	-	0.09	0.11
CH <sub>2</sub> FCl.	-	0.21	0.18	0.32

#### EXAMPLE 2.

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The procedure of example 1 was repeated but with a catalyst comprising 5% w/w palladium supported on Grade 208c charcoal. The composition of the organic products after scrubbing was as shown in Table 2.

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TABLE 2

Product	Temperature/°C.			
	210	238	282	318.
CH <sub>2</sub> F <sub>2</sub> .	7.70	18.27	36.77	35.90
CH <sub>4</sub> .	1.51	5.24	28.82	54.83
CF <sub>3</sub> H.	-	-	-	0.13
CH <sub>2</sub> Cl.	-	-	-	0.13
CH <sub>3</sub> CH <sub>3</sub> .	-	-	0.31	0.90

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## EXAMPLE 3.

The procedure of example 1 was repeated but with a catalyst comprising 10% w/w palladium supported on Grade 208c charcoal. The composition of the organic products after scrubbing was as shown in Table 3.

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TABLE 3

Product	Temperature/°C				
	217	242	262	294	326.
CH <sub>2</sub> F <sub>2</sub> .	8.74	18.83	29.67	39.53	39.25
CH <sub>4</sub> .	1.65	5.70	12.86	29.73	47.03
CF <sub>3</sub> H.	-	-	-	-	0.14
CH <sub>3</sub> Cl.	-	-	-	-	0.07
CH <sub>3</sub> CH <sub>3</sub> .	-	-	-	0.34	0.90

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## EXAMPLE 4.

The procedure of example 1 was repeated but with a catalyst comprising 15% w/w palladium supported on Grade 208c charcoal. The composition of the organic products after scrubbing was as shown in Table 4.

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TABLE 4

Product	Temperature/°C.				
	225	265	297	326	358
CH <sub>2</sub> F <sub>2</sub> .	8.13	23.78	29.30	25.62	19.98
CH <sub>4</sub> .	2.20	15.09	44.15	60.62	73.01
CF <sub>3</sub> H.	-	-	-	0.11	0.08
CH <sub>3</sub> Cl.	-	-	-	0.15	0.26
CH <sub>3</sub> CH <sub>3</sub> .	-	-	0.33	1.14	1.97

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## EXAMPLE 5.

The procedure of example 1 was repeated but with a catalyst comprising 20% w/w palladium supported on Grade 208c charcoal. The composition of the organic products after scrubbing was as shown in Table 5.

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TABLE 5

Product	Temperature/°C.			
	210	238	282	316
CH <sub>2</sub> F <sub>2</sub> .	7.7	18.3	38.8	35.8
CH <sub>4</sub> .	1.51	5.24	28.7	54.8
CF <sub>3</sub> H.	-	-	-	0.13
CH <sub>3</sub> Cl.	-	-	-	0.13
CH <sub>3</sub> CH <sub>3</sub> .	-	-	0.3	0.9

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## EXAMPLE 6.

The procedure of example 1 was repeated except that the catalyst comprised 10% w/w platinum on an active carbon (Grade 208c supplied by Sutcliffe Speakman). The composition of the organic products after 25 scrubbing was as shown in Table 6.

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TABLE 6

Product	Temperature/°C.		
	215	255	306
CH <sub>2</sub> F <sub>2</sub> .	0.18	0.82	5.94
CF <sub>3</sub> H.	0.21	0.65	0.02
CH <sub>4</sub> .	0.79	3.64	43.4
CH <sub>3</sub> Cl.	-	-	0.03

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## EXAMPLE 7.

The procedure of example 1 was repeated except that a catalyst comprising 5% w/w ruthenium on active carbon was employed (supplied by Engelhard). The composition of the organic products after 45 scrubbing was as shown in Table 7.

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TABLE 7

Product	Temperature/°C.		
	211	276	316
CH <sub>2</sub> F <sub>2</sub> .	0.27	1.46	2.15
CF <sub>3</sub> H.	0.02	0.01	0.02
CH <sub>4</sub> .	4.29	34.01	57.6
CH <sub>2</sub> Cl.	0.02	0.34	2.04
CH <sub>3</sub> F	0.02	0.04	0.02
CH <sub>2</sub> FCI	-	0.04	0.01

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## EXAMPLE 8.

20 The procedure of example 1 was repeated except that a catalyst comprising 5% w/w rhodium on an active carbon was employed. The composition of the organic products after scrubbing was as shown in Table 8.

TABLE 8

Product	Temperature/°C.		
	209	271	313
CH <sub>2</sub> F <sub>2</sub> .	0.06	4.46	8.2
CF <sub>3</sub> H.	0.01	0.12	0.08
CH <sub>4</sub> .	2.21	22.75	52.01
CH <sub>3</sub> Cl.	0.01	0.01	0.04
CH <sub>2</sub> F	-	0.01	0.02
CH <sub>2</sub> FCI	-	0.15	0.65

## 40 EXAMPLE 9.

The procedure of example 1 was repeated except that a catalyst comprising 76.6g of nickel oxide was employed. The composition of the organic products after scrubbing was as shown in Table 9.

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TABLE 9

Product	Temperature/°C.		
	212	255	312
CH <sub>2</sub> F <sub>2</sub> .	4.18	7.82	17.28
CF <sub>3</sub> H.	0.29	0.02	0.05
CH <sub>4</sub> .	8.53	18.30	36.80
CH <sub>2</sub> Cl.	0.18	1.32	9.0
CH <sub>3</sub> F	0.30	0.29	0.16
CH <sub>2</sub> FCI	-	0.02	0.10
C <sub>2</sub> H <sub>6</sub>	0.46	1.80	8.90

## EXAMPLE 10.

The procedure of example 1 was repeated except that the catalyst comprised 100ml of 5% w/w palladium on eta-alumina spheres. The flow rates of hydrogen and chlorodifluoromethane were 100ml/minute and 50ml/minute respectively. The composition of the organic product after scrubbing was as shown in Table 10.

TABLE 10

Product	Temperature/°C.	
	215	255
CH <sub>2</sub> F <sub>2</sub> .	0.24	0.96
CH <sub>3</sub> F.	0.12	0.34
CH <sub>4</sub> .	55.13	63.16
CH <sub>2</sub> Cl.	-	0.03

## EXAMPLE 11.

The procedure of example 10 was repeated but the catalyst comprised 100mls of 0.5% w/w palladium supported on eta-alumina spheres. The composition of the organic product after scrubbing was as shown in Table 11.

TABLE 11

Product.	Temperature/°C.	
	212	243.
CH <sub>2</sub> F <sub>2</sub> .	1.94	5.80
CH <sub>3</sub> F.	0.65	0.92
CH <sub>4</sub> .	37.93	55.12
CH <sub>2</sub> Cl.	1.58	1.61

In all the following examples 12 to 24, the figures given are % yields by volume.

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## EXAMPLE 12.

The procedure of example 1 was repeated except that a 40 mls of a catalyst comprising 8.2% palladium on Norit RX3 extrudate active carbon (supplied by Norit) was employed as the catalyst, and the reactor was constructed of Inconel. The composition of the organic product after scrubbing was as shown in Table 12.

TABLE 12

Product. %v/v.	Temperature/°C.					
	135	165	199	216	247	260
CH <sub>2</sub> F <sub>2</sub> .	0.3	2.1	11.7	22.4	50.3	57.0
CF <sub>3</sub> H.	0.0	0.0	0.02	0.04	0.2	0.3
CH <sub>4</sub> .	0.02	0.14	1.04	2.81	13.7	18.7
CH <sub>2</sub> FCI.	0.0	0.0	0.02	0.05	0.16	0.19
% Conversion. of CF <sub>2</sub> ClH.	0.36	2.25	12.8	25.3	64.5	76.6
% difluoromethane selectivity.	92.4	93.8	91.5	88.5	78.0	74.3

## EXAMPLE 13.

The procedure of example 12 was repeated except that a catalyst comprising 10.0% palladium on Norit RX3 extrudate active carbon (supplied by Norit) was employed. The composition of the organic product after scrubbing was as shown in Table 13.

TABLE 13

Product. %v/v.	Temperature/°C.					
	151	189	217	235	258	282
CH <sub>2</sub> F <sub>2</sub> .	1.1	2.7	6.4	17.5	31.7	50.4
CF <sub>3</sub> H.	0.0	0.0	0.01	0.04	0.1	0.2
CH <sub>4</sub> .	0.0	0.21	0.56	1.44	4.5	11.4
CH <sub>2</sub> FCI.	0.0	0.0	0.0	0.0	0.0	0.01
% Conversion. of CF <sub>2</sub> ClH.	1.1	2.91	6.97	18.98	36.3	62.0
% difluoromethane selectivity.	100.0	92.8	91.7	92.2	87.3	81.3

## EXAMPLE 14.

The procedure of example 12 was repeated except that a catalyst comprising 11.4% palladium on Grade 208c active carbon (supplied by Sutcliffe Speakman) was employed. The composition of the organic product after scrubbing was as shown in Table 14.

TABLE 14

Product. %v/v.	Temperature/°C.				
	184	219	259	280	300
CH <sub>2</sub> F <sub>2</sub> .	1.27	5.53	17.04	25.1	29.68
CF <sub>3</sub> H.	0.0	0.0	0.0	0.0	0.1
CH <sub>4</sub> .	0.63	2.63	11.5	25.7	42.81
CH <sub>2</sub> FCI.	0.0	0.0	0.02	0.04	0.06
% Conversion. of CF <sub>2</sub> CIH.	1.9	8.16	28.56	50.84	72.65

## EXAMPLE 15.

The procedure of example 12 was repeated except that a catalyst comprising 8.2% palladium on Grade 207c active carbon (supplied by Sutcliffe Speakman) was employed. The composition of the organic product after scrubbing was as shown in Table 15.

TABLE 15

Product. %v/v.	Temperature/°C.				
	162	235	273	291	306
CH <sub>2</sub> F <sub>2</sub> .	0.14	3.24	11.1	16.76	21.58
CF <sub>3</sub> H.	0.01	0.01	0.04	0.07	0.09
CH <sub>4</sub> .	0.02	0.10	8.46	16.02	25.23
CH <sub>2</sub> FCI.	0.0	0.0	0.02	0.05	0.09
% Conversion. of CF <sub>2</sub> CIH.	0.17	3.44	19.53	32.9	46.98
% difluoromethane selectivity.	86.3	72.9	56.3	50.7	45.7

## EXAMPLE 16.

The procedure of example 12 was repeated except that a catalyst comprising 8.2% palladium on SC2 active carbon (supplied by Chemivron) was employed. The composition of the organic product after scrubbing was as shown in Table 16.

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TABLE 16

Product. %v/v.	Temperature/°C.					
	172	207	243	261	277	287
CH <sub>2</sub> F <sub>2</sub> .	0.44	2.64	10.4	16.72	22.6	25.8
CF <sub>3</sub> H.	0.0	0.0	0.01	0.03	0.07	0.09
CH <sub>4</sub> .	0.08	0.82	5.81	12.43	21.3	24.3
CH <sub>2</sub> FCI.	0.0	0.0	0.02	0.04	0.09	0.15
% Conversion. of CF <sub>2</sub> ClH.	0.52	3.46	16.24	29.22	44.1	50.3
% Selectivity Difluoromethane.	85.1	76.3	63.9	57.1	51.1	51.0

## EXAMPLE 17.

The procedure of example 12 was repeated except that a catalyst comprising 8.2% palladium on SC12 active carbon (supplied by Chemivron) was employed. The composition of the organic product after scrubbing was as shown in Table 17.

TABLE 17

Product. %v/v.	Temperature/°C.				
	179	223	255	266	285
CH <sub>2</sub> F <sub>2</sub> .	0.95	6.64	16.4	21.8	29.5
CF <sub>3</sub> H.	0.0	0.01	0.03	0.05	0.11
CH <sub>4</sub> .	0.2	2.53	9.95	15.76	27.4
CH <sub>2</sub> FCI.	0.0	0.0	0.03	0.06	0.15
% Conversion. of CF <sub>2</sub> ClH.	1.15	8.18	26.05	37.67	56.85
% Selectivity Difluoromethane.	82.6	72.3	62.0	57.8	51.5

## EXAMPLE 18.

The procedure of example 12 was repeated except that a catalyst comprising 8.2% palladium on Grade 207b active carbon (supplied by Sutcliffe Speakman) was employed. The composition of the organic product after scrubbing was as shown in Table 18.

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TABLE 18

Product. %v/v.	Temperature/°C.					
	181	210	244	266	278	291
CH <sub>2</sub> F <sub>2</sub> .	0.58	1.32	6.16	11.5	22.6	24.4
CF <sub>3</sub> H.	0.02	0.01	0.01	0.04	0.02	0.01
CH <sub>4</sub> .	0.81	1.89	11.1	19.9	27.9	27.5
CH <sub>2</sub> FCI.	0.0	0.04	0.4	0.26	0.48	0.51
% Conversion. of CF <sub>2</sub> ClH.	1.41	3.26	17.67	31.7	51.0	52.4
% Selectivity Difluoromethane.	37.4	37.7	33.7	35.4	43.3	45.3

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## EXAMPLE 19.

The procedure of example 12 was repeated except that a catalyst comprising 8.2% palladium on Grade 208c active carbon (supplied by Sutcliffe Speakman) was employed. The composition of the organic product after scrubbing was as shown in Table 18.

TABLE 19

Product. %v/v.	Temperature/°C.					
	178	219	235	253	263	280
CH <sub>2</sub> F <sub>2</sub> .	0.8	5.57	11.0	18.1	23.1	30.9
CF <sub>3</sub> H.	0.0	0.01	0.02	0.03	0.05	0.1
CH <sub>4</sub> .	0.15	2.46	7.0	15.48	22.1	31.1
CH <sub>2</sub> FCI.	0.0	0.01	0.02	0.06	0.09	0.19
% Conversion. of CF <sub>2</sub> ClH.	0.95	8.05	18.04	33.67	45.3	62.3
% Selectivity Difluoromethane.	84.5	69.1	60.8	53.6	50.7	49.5

## 40 EXAMPLE 20.

The procedure of example 12 was repeated except that a catalyst comprising 8.2% palladium and 0.1% nickel on Norit RX3 extrudate active (supplied by Norit) carbon was employed. The composition of the organic product after scrubbing was as shown in Table 20.

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TABLE 20

Product. %v/v.	Temperature/°C.					
	193	228	246	267	291	309
CH <sub>2</sub> F <sub>2</sub> .	1.70	4.6	15.9	23.1	33.2	45.0
CF <sub>3</sub> H.	0.01	0.02	0.04	0.07	0.11	0.3
CH <sub>4</sub> .	0.17	0.41	1.85	3.48	5.4	23.0
CH <sub>2</sub> FCI.	0.0	0.0	0.0	0.0	0.0	0.0
% Conversion. of CF <sub>2</sub> ClH.	1.97	5.03	17.79	26.65	38.7	68.3
% Selectivity Difluoromethane.	90.9	91.5	89.4	86.7	85.6	66.0

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## EXAMPLE 21.

20 The procedure of example 12 was repeated except that a catalyst comprising 10.0% palladium and 5.0% nickel on Grade 208c active carbon (supplied by Sutcliffe Speakman) was employed, and a stainless steel reactor was used. The composition of the organic product after scrubbing was as shown in Table 21.

TABLE 21

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Product. %v/v.	Temperature/°C.			
	160	217	256	283
CH <sub>2</sub> F <sub>2</sub> .	0.24	8.14	12.35	19.59
CF <sub>3</sub> H.	0.0	0.1	0.1	0.2
CH <sub>4</sub> .	0.09	5.63	13.4	26.03
CH <sub>2</sub> FCI.	0.0	0.0	0.01	0.0
% Conversion. of CF <sub>2</sub> ClH.	0.33	13.87	25.86	45.82
% difluoromethane selectivity.	71.6	58.0	46.7	41.6

## 40 EXAMPLE 22.

The procedure of example 12 was repeated except that the reaction was conducted at a pressure of 7.5 bar. The composition of the organic product after scrubbing was as shown in Table 22.

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TABLE 22

Product. %v/v.	Temperature/°C.		
	290	315	330
CH <sub>2</sub> F <sub>2</sub> .	24.63	31.05	29.79
CF <sub>3</sub> H.	0.09	0.22	0.27
CH <sub>4</sub> .	1.76	2.50	2.64
CH <sub>2</sub> FCI.	0.06	0.06	0.07
% Conversion. of CF <sub>2</sub> ClH.	26.58	33.90	32.85
% difluoromethane selectivity.	92.7	92.8	90.8

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## EXAMPLE 23.

20 The procedure of example 10 was followed except that dichlorodifluoromethane was used instead of chlorodifluoromethane. The composition of the organic products after scrubbing was as shown in Table 23.

TABLE 23

Product. %v/v.	Temperature/°C.	
	202	232
CF <sub>2</sub> ClH.	0.28	0.12
CF <sub>2</sub> H <sub>2</sub> .	4.72	4.75
CH <sub>4</sub> .	62.89	72.11
CH <sub>3</sub> Cl.	6.19	5.68
CH <sub>2</sub> FCI.	2.13	1.48
% Conversion. of CF <sub>2</sub> Cl <sub>2</sub> .	76.32	84.14
% difluoromethane selectivity.	6.18	5.65

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## EXAMPLE 24.

The procedure of example 11 was followed except that dichlorodifluoromethane was used instead of chlorodifluoromethane. The composition of the organic products after scrubbing was as shown in Table 24.

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TABLE 24

Product. %v/v.	Temperature/°C.	
	205	245
CF <sub>2</sub> ClH.	0.23	0.43
CF <sub>2</sub> H <sub>2</sub> .	6.81	9.37
CH <sub>3</sub> .	40.66	47.98
CH <sub>2</sub> Cl.	6.64	7.62
CH <sub>2</sub> FCI.	0.78	0.36
% Conversion. of CF <sub>2</sub> Cl <sub>2</sub> .	55.35	65.92
% difluoromethane selectivity.	12.31	14.21

**Claims**

1. A process for the production of difluoromethane which comprises reacting a compound of formula XYCF<sub>2</sub> wherein X and Y are each H, Cl or Br but at least one of X and Y is an atom other than hydrogen, with hydrogen at elevated temperature in the presence of a hydrogenation catalyst.
2. A process as claimed in claim 1 wherein the compound of formula XYCF<sub>2</sub> is chlorodifluoromethane.
3. A process as claimed in claim 1 or claim 2 which comprises feeding a stream comprising the compound of formula XYCF<sub>2</sub> and hydrogen through a vessel containing the catalyst.
4. A process as claimed in any one of claims 1 to 3 wherein the temperature, pressure and catalyst composition are selected such that difluoromethane is produced with a yield of at least 20%.
5. A process as claimed in claim 4 wherein the yield is at least 30%.
6. A process as claimed in any one of claims 1 to 5 wherein the catalyst comprises palladium carried on an active carbon support.
7. A process as claimed in claim 6 wherein the loading of palladium on the support is in the range from 8% to 15% by weight.
8. A process as claimed in claim 6 or claim 7 wherein the active carbon employed is such that at a temperature of 250 °C, atmospheric pressure and a palladium loading of 10% w/w, the yield of difluoromethane is at least 50%.
9. A process as claimed in any one of claims 6 to 8 wherein the catalyst comprises one or more metals in addition to palladium carried on an active carbon support.
10. A process as claimed in claim 9 wherein the catalyst comprises a Group VIIIa metal in addition to palladium.
11. A process as claimed in claim 10 wherein the catalyst comprises palladium and nickel carried on an active carbon support.
12. A process as claimed in claim 11 wherein the proportion by weight of palladium and nickel in the catalyst is in the range from 2:1 to 500:1.
13. A process as claimed in any one of claims 1 to 12 wherein the molar proportion of hydrogen to compound of formula XYCF<sub>2</sub> is in the range from 1:1 to 4:1.

14. A process as claimed in any one of claims 1 to 13 wherein the pressure is in the range from 2 bar to 60 bar.
15. A process as claimed in any one of claims 1 to 14 wherein the temperature is in the range from 225 °C to 400 °C.
16. A process as claimed in any one of claims 1 to 15 wherein the impure difluoromethane product stream is contacted with an active carbon whereby to remove chlorine-containing impurities.

10 **Patentansprüche**

1. Verfahren zur Herstellung von Difluormethan, bei dem eine Verbindung mit der Formel XYCF<sub>2</sub>, in der X und Y jeweils für H, Cl oder Br stehen, aber mindestens einer der Substituenten X und Y für ein anderes Atom als Wasserstoff steht, mit Wasserstoff bei erhöhter Temperatur in Gegenwart eines Hydrierungskatalysators umgesetzt wird.
2. Verfahren nach Anspruch 1, wobei es sich bei der Verbindung mit der Formel XYCF<sub>2</sub> um Chlordifluormethan handelt.
3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem ein Strom, der die Verbindung mit der Formel XYCF<sub>2</sub> und Wasserstoff enthält, durch ein Gefäß geleitet wird, das den Katalysator enthält.
4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem die Temperatur, der Druck und die Katalysator-Zusammensetzung so ausgewählt sind, daß Difluormethan mit einer Ausbeute von mindestens 20 % erzeugt wird.
5. Verfahren nach Anspruch 4, bei dem die Ausbeute mindestens 30 % beträgt.
6. Verfahren nach einem der Ansprüche 1 bis 5, wobei der Katalysator Palladium auf einem Aktivkohleträger aufweist.
7. Verfahren nach Anspruch 6, wobei die Beladung des Palladiums auf dem Träger im Bereich von 8 bis 15 Gew.% liegt.
8. Verfahren nach Anspruch 6 und Anspruch 7, wobei es sich bei der verwendeten Aktivkohle um eine solche handelt, daß bei einer Temperatur von 250 °C bei Atmosphärendruck und bei einer Palladium-Beladung von 10 % G/G die Ausbeute an Difluormethan mindestens 50 % beträgt.
9. Verfahren nach einem der Ansprüche 6 bis 8, wobei der Katalysator zusätzlich zu dem Palladium auf dem Aktivkohleträger ein oder mehrere Metalle aufweist.
10. Verfahren nach Anspruch 9, wobei der Katalysator zusätzlich zu Palladium ein Metall der Gruppe VIIIa aufweist.
11. Verfahren nach Anspruch 10, wobei der Katalysator Palladium und Nickel auf einem Aktivkohleträger aufweist.
12. Verfahren nach Anspruch 11, wobei das Gewichtsverhältnis von Palladium und Nickel in dem Katalysator im Bereich von 2:1 bis 500:1 liegt.
13. Verfahren nach einem der Ansprüche 1 bis 12, wobei das Molverhältnis von Wasserstoff zur Verbindung mit der Formel XYCF<sub>2</sub> im Bereich von 1:1 bis 4:1 liegt.
14. Verfahren nach einem der Ansprüche 1 bis 13, wobei der Druck im Bereich von 2 bar bis 60 bar liegt.
15. Verfahren nach einem der Ansprüche 1 bis 14, wobei die Temperatur im Bereich von 225 °C bis 400 °C liegt.

16. Verfahren nach einem der Ansprüche 1 bis 15, bei dem der unreine Difluormethan-Produktstrom mit einer Aktivkohle in Kontakt gebracht wird, wodurch die chlorhaltigen Verunreinigungen abgetrennt werden.

#### 6 Revendications

1. Procédé de production de difluorométhane qui comprend la réaction d'un composé de formule  $XYCF_2$ , dans lequel X et Y sont chacun H, Cl ou Br, mais au moins un des X et Y est un atome autre que l'hydrogène, avec de l'hydrogène à température élevée, en présence d'un catalyseur d'hydrogénéation.
- 10 2. Procédé suivant la revendication 1, dans lequel le composé de formule  $XYCF_2$  est le chlorodifluorométhane.
- 15 3. Procédé suivant la revendication 1 ou 2, qui comprend l'alimentation d'un courant comprenant le composé de formule  $XYCF_2$  et de l'hydrogène au travers d'un récipient contenant le catalyseur.
- 20 4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel la température, la pression et la composition du catalyseur sont choisies, de sorte que le difluorométhane est produit avec un rendement d'au moins 20%.
- 25 5. Procédé suivant la revendication 4, dans lequel le rendement est d'au moins 30%.
6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel le catalyseur comprend du palladium porté sur un support de carbone actif.
- 30 7. Procédé suivant la revendication 6, dans lequel la charge de palladium sur le support se situe dans l'intervalle de 8% à 15% en poids.
8. Procédé suivant la revendication 6 ou 7, dans lequel le carbone actif utilisé est tel, qu'à une température de 250 °C, à pression atmosphérique et avec une charge de palladium de 10% p/p, le rendement en difluorométhane est d'au moins 50%.
- 35 9. Procédé suivant l'une quelconque des revendications 6 à 8, dans lequel le catalyseur comprend un ou plusieurs métaux en plus du palladium, portés sur un support de carbone actif.
10. Procédé suivant la revendication 9, dans lequel le catalyseur comprend un métal du groupe VIIIa, en plus du palladium.
- 40 11. Procédé suivant la revendication 10, dans lequel le catalyseur comprend du palladium et du nickel portés sur un support de carbone actif.
12. Procédé suivant la revendication 11, dans lequel la proportion en poids de palladium et de nickel dans le catalyseur se situe dans l'intervalle de 2:1 à 500:1.
- 45 13. Procédé suivant l'une quelconque des revendications 1 à 12, dans lequel la proportion molaire d'hydrogène au composé de formule  $XYCF_2$  se situe dans l'intervalle de 1:1 à 4:1.
14. Procédé suivant l'une quelconque des revendications 1 à 13, dans lequel la pression se situe dans l'intervalle de 2 bars à 60 bars.
- 50 15. Procédé suivant l'une quelconque des revendications 1 à 14, dans lequel la température se situe dans l'intervalle de 225 °C à 400 °C.
16. Procédé suivant l'une quelconque des revendications 1 à 15, dans lequel le courant produit de difluorométhane impur est mis en contact avec un carbone actif pour éliminer les impuretés contenant du chlore.